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(54) Low toxicity drilling fluids

(57) Oil-containing drilling fluids for use in drilling wells into the earth include a non-toxic oil component comprising a hydrocarbon distillate fraction which is essentially free of aromatic components and which contains at least 80 and preferably at least 90 volume percent iso-aliphatics. This fraction, which is preferably a heavy alkylate or an olefin oligomerization product, may be blended with a high-boiling component which is essentially free of aromatics boiling below 315°C. Solvent refined lube stocks are useful for this component. The volume ratio of the two components is generally from 100:0 to 30:70, preferable 80:20 to 40:60. Drilling fluids of this type are less toxic to many life forms, especially marine life forms.

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SPECIFICATION

Low toxicity drilling fluids

This invention relates to drilling fluids which may be used in the drilling of wells extending into subterranean mineral bearing formations, for example, oil or gas containing formations.

The rotary system of drilling wells into the earth to reach subterranean formations, for example, oil and gas bearing formations, requires the circulation of a drilling fluid or drilling mud in order to remove the drilled cuttings from the bottom of the hole to keep the bit and the bottom of the hole clean. In addition, the fluids help to contain well pressure when drilling through pressured formations and also to lubricate the drill stem and to cool the bit. Water-based fluids are cheaper and less toxic than fluids which contain oil but in certain geological formations, oil-based drilling fluids offer better borehole stability and drill lubrication. Thus, the use of oil-based drilling fluids may be indicated in formations such as oil sands which are damaged by water or by the filtrate from water-based muds and in formations where damage may result from the swelling of clay particles in the pores of a sandstone matrix so that oil or other formation fluids cannot readily flow through the sand and into the wellbore. Another type of damage which may result from the use of water-based fluids occurs when water invades a formation for a considerable distance from the wellbore and, in rocks of low permeability, drastically reduces the fluid conductivity of the rock in the presence of both oil and water in the small pores. Although the use of salt water will reduce the swelling of any clays which may be present, the use of oil based drilling muds may be required.

Oil based muds are suspensions of solids in oil. High flash point diesel fuel oils (ASTM D 975) are commonly used as the liquid phase and the necessary finely dispersed solid may be obtained by adding oxidized (air blown) asphalt. Common weighting agents may be used to increase the density and the viscosity and thixotropic properties may be controlled by special soaps and other chemicals of known kinds. Oil based muds are particularly useful for purposes such as preventing the caving of certain shales and particularly, as completion muds for drilling into sensitive sands which are damaged by water. Other oil-containing muds are oil emulsion muds, commonly of the oil-in-water type, in which small droplets of oil are dispersed in a continuous water phase. The amount of oil may vary up to 50% of the volume of the mud, although only 10 to 15% is commonly oil. Clays and other minerals and common mud-treating chemicals act as emulsifying agents and additional emulsifiers such as soaps may also be used. Inverted emulsions of the water-in-oil type have also been developed, principally for well completion purposes, and in these muds, oil is the continuous phase with water present in the form of small droplets. Special soaps and surfactants of known types may be required in their preparation. These muds offer excellent borehole stability, are stable under conditions of high temperature and pressure and are generally not affected by salt, grease, and hydrite or cement contamination.

One problem encountered with all diesel fuel containing drilling muds, however, is toxicity to many life forms. Although the mud itself is recirculated after removal of drill cuttings, the cuttings become contaminated with the oil and environmentally safe disposal methods are therefore required. In offshore drilling operations, environmentally safe disposal may require extensive washing or calcining to remove the oil or transport of the cuttings onshore for land disposal. It would be desirable to avoid these alternatives which are all relatively expensive and to use an oil which has a low toxicity to aquatic life so that the cuttings may be safely discharged into the sea. The use of a low toxicity drilling mud would also be desirable in land drilling because disposal problems would again be minimized.

Proposals have been made for the preparation of low toxicity drilling muds using special base oils, for example, certain highly refined white mineral oil products which are naphthenic in nature. SPE Paper No. 11891/3, prepared for the Offshore Europe 83 Conference in conjunction with the meeting of the Society of Petroleum Engineers of AIME, Aberdeen, Scotland, 6–9 September 1983, describes muds of this type. These muds have, however, been expensive to produce since they require special base stocks and extensive refining in order to secure the desired low toxicity. It would therefore be desirable to formulate oil-containing drilling muds based on commonly available refinery stocks without the need for extensive and costly refining procedures.

W have now found that certain, readily available refinery products such as heavy alkylate fractions, alone or in combination with high boiling solvent raffinates such as lube oil base stocks, are satisfactory oils for oil containing drilling fluids and ar much less toxic to aquatic life than diesel fuel.

According to the present invention, an oil-containing drilling fluid for us in drilling wells into the earth, includes an il component comprising a non-aromatic hydrocarbon fraction which is essentially free of aromatic components and which has an iso-aliphatic content of at least 80% by volume. The oil component desirably has a Flash Point (ASTM D 93) of at least 60°C (140°F)

preferably at least 65°C (150°F) for safety reasons and should hav a P ur Point (ASTM D97) no higher than −5°C (23°F) for use in cold weather environments such as the North Sea although higher pour points may be tolerated in warmer conditions such as the Gulf of Mexico. This non-aromatic fraction may be used either on its own in the drilling mud or in combination with a second hydrocarbon component, preferably a high-boiling solvent raffinate, which is essentially free of aromatic components boiling below 315°C (600°F). The non-aromatic fraction will generally constitute 30 to 100, preferably 40 to 80 volume percent of the oil components of the mud while the other component will constitute the complementary amount, up to 70, preferably not more than 60, volume percent of the oil in the mud.

The oil component is formulated into a drilling mud of the appropriate properties, having regard to the conditions of use, with drilling mud ingredients such as surfactants, clays, weighting agents and stabilizers. The muds may be formulated as oil-based muds, emulsions or invert emulsions, as is desired.

Generally, the toxicity of mineral oils to aquatic and other life may be attributed to aromatic components. The non-aromatic fractions which are used in the present oil-containing drilling fluids are essentially free of aromatics and therefore are of low toxicity to aquatic and other forms of life. However, these non-aromatic fractions may not be wholly satisfactory for a number of reasons. First, they may be unsuitable for other purposes, for example, use as a diesel fuel and second, in certain cases, the drilling mud may require re-formulation if it is to be wholly stable and otherwise satisfactory. We have found, however, that the effective aquatic toxicity of aromatic oils arises from the solubility in water of the aromatic hydrocarbons and that low boiling aromatic compounds are much more water soluble than high boiling ones. If the aromatic components of an oil have a sufficiently high boiling point, generally above 315°C. (600°F.), the water solubility is sufficiently low that a low effective aquatic toxicity results. Lube oil base stocks and other high boiling solvent raffinates in which any aromatic components boil above 315°C. (600°F.) are therefore suitable for blending with the non-aromatic fraction in order to improve certain other properties of the oil including its compatibility with the clays and polar components of certain drilling mud formulations. Although these high boiling fractions may still contain substantial amounts of aromatics, e.g., up to about 35% by weight, the aromatic content will be high boiling and of low solubility in water and therefore unobjectionable from the point of view from aquatic toxicity. Lube oil base stocks of this kind could be used as base oils for low toxicity drilling fluids from the point of view of their aquatic toxicity, but they are generally too viscous for making satisfactory drilling fluids. However, when blended with the relatively lower boiling, non-aromatic fraction, an oil with physical properties such as viscosity and boiling range similar to diesel fuel can be produced but with very low aquatic toxicity. In addition, because the physical properties of the blended oils can be controlled by the blending, these oils can be formulated to have satisfactory combustion performance in diesel engines and gas turbines and could therefore be used as emergency power fuels on drilling platforms. The non-aromatic component on its own may in certain cases be unsatisfactory as a diesel fuel because of its low cetane number but blending with the other components can produce a satisfactory fuel for this purpose.

Non-aromatic Component

The non-aromatic component of the drilling mud oil is a hydrocarbon in the distillate boiling range which, for safety reasons, is selected to have a Flash Point (ASTM D 93, Pensky-Martin Closed Cup) of at least 60°C (140°F), preferably at least 65°C (150°F), so as to permit relatively risk-free use under normal drilling conditions.

This component of the oil is characterized by being essentially free of aromatic components which would be toxic to marine life. In addition, it will have an iso-aliphatic content of at least 80%, and preferably at least 90%, by volume. The term "iso-aliphatic" is used here and elsewhere in this specification to refer to aliphatic compounds, particularly paraffins and olefins with one or more chain branchings, e.g., paraffins which are not *n*-paraffins, and olefins which are not n-olefins. The iso-aliphatic content of this fraction may therefore be provided by iso-paraffins, iso-olefins or mixtures of the two. Hydrocarbon fractions of this type may be produced by various processes but a convenient source is the refinery product sream obtained from an alkylation unit. Another source of these fractions in the oligomerization of olefins over acidic catalysis, especially the intermediate pore size zeolite ZSM–5.

Alkylation is a conventional petroleum refinery process by means of which an iso-paraffin typically iso-butane is combind with an olefin to form a higher boiling iso-paraffin of impr v d properties. The ommercial application of the process is largely confined to the alkylation of lower alkan s, sp cially iso-butane, with lower alkenes such as pr pylene, butylene or pentene, or mixtures of these olefins, using an acidic catalyst, generally sulfuric acid or hydrofluoric acid. During the alkylation reaction, the paraffin is c nverted to branched-chain paraffins. The alkylation product is therefore an excellent source of iso-paraffins for use in the present drilling muds.

Various alkylation processes are described in Advances in Petrol um Chemistry and Refinery,

Ed. J. J. McKetta, Interscience New Y rk 1964, Vols. I (p. 336 et seq.), II (p. 314 et seq.) and III (p. 278 et seq.), to which reference is made for a description of typical alkylation processes which may be used to produce highly iso-paraffinic fractions which may be used in the present drilling muds.

The heavy alkylate product from the alkylation unit, i.e., the fraction boiling above the gasoline range, is used for the present purposes in order to obtain the desired Flash Point. Generally, therefore, the heavy alkylate fraction will have an initial boiling point of at least 150°C (about 300°F), preferably at least 170°C (about 340°F). The final boiling point is typically from 315°C (about 600°F) to 345°C (about 650°F), depending upon the alkylation process in use and the purposes for which the product is otherwise intended. The boiling ranges in themselves are not critical but will generally follow upon the selection of a fraction which complies with the Flash Point requirement which should be observed for safety in use.

Another essentially non-aromatic hydrocarbon fraction which may be used is the product obtained by oligomerizing low molecular weight olefins over acidic intermediate pore size zeolites such as ZSM–5. A preferred process of this kind is known as Mobil Olefins to Gasoline/Distillate (MOGD) process and in the MOGD process, low molecule weight olefins, particularly C_2 to C_5 alkenes, are passed over an acidic intermediate pore size zeolite such as HZSM–5 at moderately elevated temperatures and pressures. The oligomerization products are liquid fuels in the gasoline and distillate boiling range which may be separated by distillation to produce distillate range products which may be used in the present compositions.

The olefinic feed to the MOGD process consists essentially of C_2 to C_8 aliphatically unsaturated hydrocarbons containing a major fraction of mono-alkenes, with dienes and other deleterious materials being essentially absent. The feedstock is preferably at least 50 to 75 mole percent C_3 to C_5 alkenes, preferably ethylene, propylene and butylene. Feedstocks of this kind may be obtained from various sources including fossil fuel processing streams, effluent from gas separation units, pyrolysis of C_2+ hydrocarbons, and various synthetic fuel processing streams. Olefinic effluents from the fluidized catalytic cracking of gas oil and other heavy oil fractions is a valuable source of olefins, mainly C_3 to C_4 olefins for conversion to gasoline and distillate range products by the MOGD process.

The feedstock may be combined with liquid recycle from the oligomerization process as a diluent and following pressurization, is passed to a catalytic reactor in which the oligomerization occurs. The reactor is suitably comprised of a number of fixed bed reactors with a heat exchange system for maintaining the desired thermal balance. The reactor effluent may be cooled by heat exchange, after which the product may be split to obtain a gasoline fraction and a distillate faction. The distillate range fraction is the one which is used in the formulation of the present low toxicity drilling fluids in order to obtain the desired minimum Flash Point, although boiling range in itself is not critical. The distillate range fraction will, however, typically have an initial boiling point of at least 150°C (about 300°F), more usually at least 165°C (about 330°F) with an end boiling point below 400°C (about 750°F). The gasoline fraction may be used to provide recycle diluent, as described in U.S. Patents Nos. 4,456,779, 4,450,311 and 4,444,988.

The catalyst used in the oligomerization process is an acidic intermediate pore size zeolite such as ZSM–5 although other zeolites having a Constraint Index from 1 to 12 such as ZSM–11, ZSM–12, ZSM–23, ZSM–35, ZSM–38, ZSM–48 and the ZSM–5/ZSM–11 intermediate may also be used. Zeolites of this type will also have a silica to alumina pore ratio (structural) of at least 12:1 and preferrably much higher, generally at least 30:1 or even higher, e.g., 70:1, 200:1, 500:1 or even higher. In principle, the upper limit of silica to alumina mole ratio appears to be unbounded and in some intermediate pore size zeolites may be as high as 30,000:1 or even higher, extending at least theoretically to infinity. The significance of the term "Constraint Index" is described in U.S. Patent 4,456,779 to which reference is made for a definition of this Index and of the method by which it may be determined. Zeolite ZSM–5 is described in U.S. Patent No. 3,702,886, the ZSM–5/ZSM–11 intermediate in U.S. Patent No. 4,229,424, ZSM–11 in U.S. Patent No. 3,709,979, ZSM–12 in U.S. Patent No. 3,832,449, ZSM–23 in U.S. Patent No. 4,076,842, ZSM–35 in U.S. Patent No. 4,016,245, ZSM–38 in U.S. Patent No. 4,046,859 and ZSM–48 in U.S. Patent No. 4,397,827. U.S. Patent Re No. 29,948 describes a crystalline material having an x-ray defraction patent of ZSM–5 and U.S. Patent No. 4,061,724 describes a high-silica ZSM–5. Reference is made to these patents for a description of these zeolites, their properties and methods of pr paration.

The process conditions and equipment suitable for carrying out th oligomerization are described in U.S. Patents Nos. 4,456,779, 3,960,978, 4,021,502, and 4,150,062, to which reference is made for details of such conditi ns, catalyst and equipment. Gen rally, the conditions used in distillate mod op ration (i.e., to optimize distillate production) ar of moderately elevated temperature, typically 190° to 315°C. (375 to 600°F.), with a maximum temperature differential across any one react r in the preferred multibed sequence of about 10°C. (50°F.). Space velocities will generally range from 0.1 t 5, pref rably 0.5 to 1 (LHSV based on olefin

feed). Pressures will generally range from 3500 to 7,000 kPa, (about 500 to 1,000 psig) alth ugh pressures above and below this range should n t b excluded.

A preferred heat exchange technique for maintaining the desired thermal balance in the systems is disclosed in U.S. Patent No. 4,450,311 to which reference is made for a description of the technique. Other preferred methods of operating the MOGD process are described in U.S. Patents Nos. 4,433,185, 4,444,988 and 4,456,779 to which reference is made for a description of such preferred procedures.

The distillate boiling range product of the MOGD process is rich in iso-olefins, typically containing at least 80% and usually at least 90% by volume iso-olefins, the balance being essentially iso-paraffins. The distillate product may be used directly as the non-aromatic component of the drilling mud oil or, alternatively, may first be subjected to a hydrogenation treatment to convert the iso-olefins to iso-paraffins, so that the hydrogenated product will be almost entirely iso-paraffins. Hydrogenation is suitably carried out over a metal catalyst, suitably a metal of Group VI or VIII of Periodic Table, e.g. Ni, Co, Mo or W on an inert support of low acidity, e.g. alumino or silica, under conditions of elevated temperature and pressure, for example, 100° to 550°C (212° to 1022°F) at pressures of 150 to 3000 kPa (21 to 420 psig). The product of the MOGD process, whether hydrogenated or not, is essentially free of n-paraffins and therefore provides a low Pour Point without the necessity of using Pour Point improvers for cold weather application.

Heavy Oil Component

Although the highly iso-aliphatic fraction may be used on its own as the oil component of the mud, it may be desirable to blend it with a second hydrocarbon component in order to obtain the best combination of properties. Two factors are relevant here. First, on offshore drilling rigs, it is desirable to minimize the number of different oils which need to be stored, especially when large quantities of them are required. When diesel oil based muds were used, one supply of oil could obviously supply the diesel equipment on the platform as well as providing oil for formulating the mud. The heavy alkylate fractions, on their own, may be unsatisfactory diesel fuels because their Cetane Number (ASTM D 613) may be too low (by contrast, however, the heavy MOGD fraction may be satisfactory as a diesel fuel). Both these problems may, however, be overcome by blending the highly iso-aliphatic component with the heavy oil fraction which will supply sufficient high boiling components to provide satisfactory Cetane Number for diesel fuel blending but still preserve the low toxicity characteristics of the blend as a whole. As previously mentioned, we have found that the toxicity of hydrocarbons to marine life derives from the solubility in water of low boiling aromatics. By contrast, aromatics boiling over 315°C (600°F) have a sufficiently low solubility in water that they are essentially non toxic to marine life. The presence of these high boiling aromatics in therefore acceptable from the viewpoint of toxicity while, at the same time, providing an optimal combination of properties in the entire oil blend.

Second, the use of the wholly aliphatic fraction may require certain drilling muds to be reformulated if the mud is to be completely stable and otherwise satisfactory. The necessity for re-formulation may, however, be avoided if the high boiling component is added. The high boiling component, therefore, is characterized by being essentially free of aromatic components boiling below 315°C (600°F), preferably 345°C (about 650°F). This component which complementarily makes up the oil blend will generally be present in an amount up to 60, preferably not more than 40, volume percent of the oil in the blend. Generally, the initial boiling point of this component will be at least 315°C (600°F), more usually 345°C (about 650°F), with a typical end boiling point below 650°C (about 1200°F), usually below 540°C (about 1000°F), although these boiling points are not critical and wider boiling ranges may readily be accepted, e.g., an IBP as low as 250°C (about 480°F) or 270°C (about 520°F) provided that the limitation on low boiling aromatics is observed. A convenient source of this high boiling component is a high boiling solvent raffinate such as a lube oil base stock. Other high boiling components including dewaxed lube stocks obtained by solvent or catalytic dewaxing and other fractions essentially free of low boiling aromatics may also be used.

These lube oil base stocks may be paraffinic, naphthenic or asphaltic in nature but it is normally preferred to use paraffinic stocks both from the point of their commercial availability and their physical properties such as viscosity and viscosity index. In addition, paraffinic lube stocks will generally be free of substantial quantities of aromatic (asphaltic) components and th r fore will b of inherently low r toxicity than the more asphaltic materials. However, the presence of substantial amounts of aromatic components may be tolerated provided that they are high boiling (above 315°C.) so that the solubility of these aromatic components in water is minimiz d. A preferred technique for removing aromatic components from base stocks is by furfural xtraction and this will generally be effective to remove the lower boiling, undesirable aromatics. After furfural xtraction, the lube oil base stocks may still typically contain up to about 35% aromatics but becaus the residual aromatics will be high boiling, they will hav low aquatic toxicity.

Normally, the volume ratio of the iso-paraffinic compon nt to the high boiling component stock will be from 100:0 to 30:70, preferably 80:20 to 40:60, and advantageously from 60:40 to 70:30. In each individual case, however, the exact ratio chosen should be selected according to the properties desired in the oil blend and in the final drilling mud and the properties of the oil stocks available. For example, if the expected conditions during drilling include high temperature, it may be desirable to include a relatively higher proportion of the high boiling lube oil base stock with relatively less of the lower boiling distillate range fraction. Also, if an MOGD stock is available and mud formulation is no problem, there may be no need to blend in the high boiling component. Similarly, if diesel performance is not required there may again be no need to include the high boiling component.

The oil component of the drilling fluid should, whe formulated, have a Flash Point (ASTM 93) of at least 60°C (140°F), preferably at least 65°C (150°F) for safety reasons, as previously mentioned: because the optional high-boiling component of the oil will not contain substantial quantities of volatiles which contribute to a low Flash Point, it will not generally need to be individually monitored for compliance with this requirement although the iso-aliphatic component, being in the distillate boiling range obviously will be. Also, when the mud is to be used in cold weather environments such as the North Sea, a Pour Point (ASTM D 97) of −5°C (23°F) maximum, and preferably not above −12°C (10°F), should be observed in order to minimize handling and pumping problems when the oil is being stored prior to mixing with the other components of the mud. Typically, a Pour Point of −20°C (−5°F) will be suitable for use in most environments. However, if included for use in warm weather environments, the Pour Point restriction may be relaxed because there will then be little risk of pumping problems.

Drilling Fluid Formulation

The oil containing drilling fluids which contain the iso-aliphatic distillate range fractions, either on their own or together with the lube base stocks, may be oil-based fluids, oil-in-water emulsions or inverted emulsions. The invert emulsion muds will often be preferred because of their stability in many applications. The components of the drilling fluid other than the oil are those which would normally be employed in the appropriate type of mud and will generally be of commercially available types prepared according to the prescriptions of the supplier. Typical components of the oil based muds will include oxidized asphalts, clays and other conventional materials. Oil-in-water emulsions will generally contain clays, e.g., surface-modified (organic) bentonite clays, other minerals and common mud treating chemicals as emulsifying agents and stabilizers, e.g., high temperature stabilizers. Inverted emulsions will normally include the special soaps and surfactants required for their preparation. In each case weighting agents such as barite may be present if operating conditions require. Generally, no adaptations of the conventional mud formulae are required when replacing the diesel fuel oils of conventional formulations with the hydrocarbon components according to the present invention although, obviously, the non-oil components should themselves be selected to be of the requisite low toxicity. Low toxicity mud packages are commercially available from a number of suppliers.

A typical drilling mud formulation, for example, comprises the following low toxicity components:

Primary emulsifiers, kg.	9
Secondary emulsifier, kg.	2
Lime, kg.	5
High temperature stabilizer, kg.	8
Organic bentonite, kg.	3
Barite, kg.	214
Calcium chloride, kg.	37.2
Water, kg.	32
Oil, kg.	74

Because the oils of the present invention have a lower aquatic toxicity, as compared to conventional diesel fuels, the cuttings contaminated with the oils are of markedly lower toxicity to various life forms, especially marine forms of life. Cuttings contaminated with the oils may therefore be more easily disposed of than cuttings contaminated by conventi nal oil-containing drilling fluids. This is a particular advantage in offshor operations, as previ usly mentioned. In addition, these oils may also be blended to have satisfactory combustion performance in diesel engines, gas turbines and multi-fuel engines which may be us d on drilling equipment, specially on ffshore rigs and they may ther fore be employed where needed f r fuel.

Examples 1–3

In Examples 1 to 3, thr e drilling fluids were f rmulated with the objective of meeting the target properties set ut in Table 1 bel w:

Table 1
Drilling Fluid Target Properties

	U.S. Gulf Formations	North Sea Formations
Plastic Viscosity, cp	30–45	38–52
Yield Point, lb/100 ft²	12–18	19–25
Gel Strength, lb/100 ft²	3	12–18
Electrical Stability, volts	600–700	250+
Comments	15 cm. Borehole	45 cm. Borehole

Note:
Properties at 46°C. (115°F.)

The three formulations were prepared using a heavy alkylate fraction having an initial boiling point of 182°C. (360°F.) obtained by H_2SO_4 alkylation and a 60 SUS (approx. 10 cs) solvent refined lube oil base stock essentially free of low boiling (below 315°C) aromatic components. These oils were formulated with commercially available drilling mud components to produce drilling muds having properties as close as possible to the target properties. Because the muds were not optimized for drilling fluid performance, the performance ratings reported below are subject to further improvement. The properties of the muds are given in Table 2 below:

Table 2
Drilling Fluid Performance

	Example No.		
Oil	1 Alkylate	2 60% Alkylate 40% Lube	3 60% Alkylate 40% Lube
Formulation	Environmul w/Geltone II	NL Baroid Environmul	Milchem Carbo S.E.A.
Plastic Viscosity, cp.	28	22	38
Yield Point, lb/100 ft²	11	11	41
Gel Strength, lb/100 ft²	5	5	32
Electrical Stability, volts	—	2000+	2000+
Comments	Good Performance	Good Performance	Good Performance

Note:
1. Properties at 46°C. (115°F.)
2. All proportions by weight
3. Geltone, Baroid, Milchem, Carbo SEA are trademarks

Toxicity Testing

Various oils, including the heavy alkylate and the lube stock of Examples 1–3, were tested for aquatic toxicity by a test procedure based upon the guidelines of the United Kingdom Ministry of Agriculture, Fisheries and Food, Directorate of Fisheries Research, March 1982. Briefly, the base oil under investigation is dispersed into the medium surrounding the selected aquatic species. Brown shrimp *(Crangon crangon)* is selected as the species because of its established sensitivity to marine pollution.

In the test, the test speci s ar first acclimatized to the t st m dium for at least nine days at a t mp rature f 14°–17°C with aeration at greater than 80% air saturation valu . An initial 48-hour period for settling-in is provided to determine species batch acceptability based upon mortality during this period. The medium is synthetic seawat r (Aquarium Systems, Inc.) at salinity greater than 28 0/00, circulated through gravel and carbon filt rs. After acclimatization, the species are loaded into 50 l. glass aquaria containing 40 l. synthetic sea water at a loading of 20 shrimp per vess l (approx. 1 litre per gram shrimp). T mperature is held at 14°–17°C for the 96-hour duration f the test with a light regime of 16 hr light, 8 hr dark. Aeration is

maintained at greater than 80% air saturati n value via narrow glass tubing. Test media are renewed daily. The test oils are dispersed in the sea water without the aid of surfactants, dispersant or additional solvents; dispersal is maintained by means of continuous mechanical agitation. Animals are inspected frequently during the first six hours of the test and thereafter, at least at daily intervals. Abnormal appearance or behavior is noted and dead animals removed on observation. A mortality of greater than 20% in the control vessel (synthetic sea water, no test substance) invalidates the test.

Test concentrations of 10, 33, 100, 333, and 1000, 3333 and 5000 mg./l. are used to determine LC_{50}, the lethal concentration of the oil in water that results in 50% mortality for the specified life forms. The LC_{50} values may be calculated from observed mortalities using techniques such as those described in Probit Analysis, 3rd Ed., Finney, D.J., Cambridge University Press 1971 or J. Pharmac. Exp. Ther. *96;* 99 (Litchfield, J. T.; Wilcoxon, F.).

The results are given in Table 3 below:

Table 3
Aquatic Toxicity

Oil	(1) 96-Hour LC_{50}, mg/l
Diesel Oil (2)	7–12
MOGD Distillate	5000
Heavy Alkylate (HF Catalyst) (3)	5000
Heavy Alkylate (H_2SO_4 Catalyst) (3)	1800
60 SUS Lube Stock A	1900
60 SUS Lube Stock B	1000
100 SUS Lube Stock (Catalytic Dewaxed)	5000
100 SUS Lube Stock (Solvent Dewaxed)	5000
150 SUS Lube Stock	5000
Blend: 60% 360°F+ Heavy Alkylate 40% 60 SUS Lube Stock	3300

Notes:
(1) Lethal concentration for 50% mortality of Crangon shrimp after 96 hours of continuous exposure.
(2) ASTM Standard Specification Grade 2 Diesel Oil (ASTM D975)
(3) IBP 182°C (360°F).

Marine fish (juvenile plaice) were also tested with the 60% heavy alkylate/40% 60 SUS lubestock blend. The 96-hour LC_{50} with juvenile plaice was greater than 3300 mg/l, and at the maximum 3300 mg/l tested dosage, the juvenile plaice were less sensitive to the oil than Crangon shrimp.

CLAIMS

1. A drilling fluid for use in drilling wells into the earth having an oil component comprising an iso-aliphatic hydrocarbon oil which is essentially free of aromatic components and which has an iso-aliphatic content of at least 80 percent by volume.

2. The drilling fluid according to Claim 1 wherein the iso-aliphatic hydrocarbon oil has a boiling range within the range of 150° to 345°C.

3. The drilling fluid according to Claim 1 or 2 wherein the iso-aliphatic hydrocarbon oil has a flash point of at least 60°C.

4. The drilling fluid of Claim 1, 2 or 3 wherein the iso-aliphatic hydrocarbon oil comprises an olefin oligom r.

5. Th drilling fluid of Claim 4 wherein the olefin oligomer comprises a hydrog nated lefin oligomer having an iso-paraffin content of at least 80 p rcent by volum .

6. The drilling fluid of Claim 4 wherein the lefin oligomer has an iso-olefin content of at least 80 perc nt by volume.

7. Th drilling fluid of Claim 4 wher in the olefin oligomer is produced by the oligomerization of C_2 to C_5 aliphatically unsaturated hydr carbons containing a major fraction of mono-alk nes ov r an acidic, intermediat por size z olite at elevated temperature and pressure.

8. The drilling fluid of Claim 1 wherein the oil component further comprises a high boiling hydrocarbon oil compon nt which is ssentially free of aromatic c mponents boiling below 315°C.

9. The drilling fluid of Claim 8 wherein the volume ratio of the iso-aliphatic hydrocarbon oil to the high boiling hydrocarbon oil is from 100:0 to 30:70.

10. The drilling fluid of Claim 8 which has a pour point of −50°C maximum.

11. A process of rotary drilling oil and gas bearing wells comprising using a drilling fluid which comprises an oil component including an iso-aliphatic hydrocarbon oil having an iso-aliphatic content of at least 80 percent by volume, the iso-aliphatic hydrocarbon oil being essentially free of aromatic components.

12. The process of Claim 11 wherein the iso-aliphatic hydrocarbon oil has a boiling range within the range of 150° to 345°C.

13. The process of Claim 11 or 12 wherein the iso-aliphatic hydrocarbon oil has a flash point of at least 60°C.

14. The process of Claim 11, 12 or 13 wherein the iso-aliphatic hydrocarbon oil comprises an olefin oligomer.

15. The process of Claim 14 wherein the olefin oligomer is produced by the oligomerization of C_2 to C_5 aliphatically unsaturated hydrocarbons containing a major fraction of mono-alkenes over an acidic, intermediate pore size zeolite at elevated temperature and pressure.

16. The process of Claim 14 wherein the olefin oligomer comprises a hydrogenated olefin oligomer having an iso-paraffin content of at least 80 percent by volume.

17. The process of Claim 14 wherein the olefin oligomer has an olefin content of at least 80 percent by volume.

18. The process of Claim 11 wherein the oil component of the drilling fluid further comprises a high boiling hydrocarbon oil component which is essentially free of aromatic components boiling below 315°C.

19. The process of Claim 18 wherein the volume ratio of the iso-aliphatic hydrocarbon oil to the high boiling hydrocarbon oil is from 100:0 to 30:70.

20. The process of Claim 18 wherein the drilling fluid has a pour point of −5°C. maximum.

21. A process of rotary drilling oil and gas bearing wells comprising utilizing a drilling fluid which comprises an oil component having a flash point of at least 60°C., the component including 30 to 100 percent of an iso-aliphatic hydrocarbon having a flash point of at least 60°C. and an iso-aliphatic content of at least 80 volume percent and from 0 to 70 percent of a high boiling hydrocarbon oil which is essentially free of aromatic components boiling below 315°C., the percentages being by volume, based on the total volume of the oil component.

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